REPORT DOCUMENTATION PAGE

Form Approved OMB No. 074-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget Paperwork Reduction Project (07/04-0189) Washington DC 20503

AGENCY USE ONLY (Leave blank)	2. REPORT	3. REPORT TYPE ANI		
4. TITLE AND SUBTITLE	DATE 1996	Scientific paper pre	sented 14-19 July 5. FUNDING	
Laser induced fluorescence spectroscopy for in-situ	u detection of petrol	leum contamination	N/A	
6. AUTHOR(S) D.S. Knowles. S.H. Lieberman, M. Davey, & B. W	Vingfield			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		8. PERFORMING ORGANIZATION		
Naval Command, Control & Ocean Surveillance Center 53475 Strothe Rd. San Diego, CA 92152	Computer Science 4050 Hancock Str San Diego, CA 92	reet	REPORT NUMBER N/A	
	University of Cal- San Diego, CA	lifornia, San Diego		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203			N/A	REFORT NORDER
11. SUPPLEMENTARY NOTES Scientific paper presented at the 1996 XX Internat in part by SERDP. The United States Governmen contained herein. All other rights are reserved by the state of th	t has a royalty-free	license throughout the		
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution is unlimited			12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 Words)		-		<u> </u>
A fiber-optic chemical sensor has been developed field detection of underground petroleum contamin improved performance, particularly at detecting light	nation. Recent expe	eriments using a 308 nm		
			AAA7	40 007

19980710 007

14. SUBJECT TERMS			15. NUMBER OF PAGES
SERDP, Petroleum contamination, Laser induced f	4		
			16. PRICE CODE N/A
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclass.	OF THIS PAGE	unclass.	UL
	unclass.		

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89) Prescribed by ANSI Std. Z39-18 298-102

Laser induced fluorescence spectroscopy for *in-situ* detection of petroleum contamination

59 - 1996

David S. Knowles & Stephen H. Lieberman

Naval Command, Control & Ocean Surveillance Center

53475 Strothe Rd.

San Diego, CA 92152

(619) 553-1281 (phone)

(619) 553-2876 (Fax)

dknowles@nosc.mil

Michele Davey

Computer Sciences Corp.

4045 Hancock St.

San Diego, CA 92110

Blair Wingfield
University of California, San Diego
San Diego, CA

Abstract

A fiber-optic chemical sensor has been developed using laser induced fluorescence (LIF) to provide high resolution, real-time, in-situ field detection of underground petroleum contamination. Recent experiments using a 308 nm XeCl laser source have shown improved performance, particularly at detecting light molecular weight (i.e. aviation) fuels.

Laser induced fluorescence spectroscopy for *in-situ* detection of petroleum contamination

David S. Knowles* & Stephen H. Lieberman Naval Command, Control & Ocean Surveillance Center 53475 Strothe Rd. San Diego, CA 92152

> Michele Davey Computer Sciences Corp. 4045 Hancock St. San Diego, CA 92110

Blair Wingfield University of California, San Diego San Diego, CA

Fuel storage tanks, hidden underground at sites such as gasoline stations and airports throughout the world, are leaving an unexpected legacy: the soil beneath the tank is often heavily contaminated with toxic hydrocarbons that may have been leaking for decades.[1] Studies have shown that certain components of fuels are carcinogenic, and while natural bacteria will slowly degrade most hydrocarbons, the carcinogenic compounds can remain in the ground long after the source has been removed.

The need for rapid assessment of such sites has led to the development of spectroscopic systems that are capable of remotely measuring the presence of underground petroleum contamination. [2-4] These systems use laser induced fluorescence (LIF) to detect the presence of petroleum products by exciting fluorescence in a component of most petroleums, the polynuclear aromatic hydrocarbons (PAHs). The PAHs are typically excited in the UV, in our case using a 337 nm nitrogen laser, and the emission is characteristically Stokes shifted towards the visible [5]. Because petroleum compounds are a complex mixture of different PAHs (along with a large range of alkanes, cycloalkanes and other organic compounds), the emission spectrum is a convolution of a large number of individual molecular spectra. While it is not possible to deconvolve the measured spectrum to determine the exact composition of the contaminant, the spectral shape of the

[Knowles, Lieberman, Davey, Wingfield, "Laser-Induced fluorescence spectroscopy..."]

emission does provide information on the class of fuel that may be present underground, and the intensity of the fluorescence is related to the concentration of the contamination.[6]

We have recently begun experiments using a 308 nm XeCl laser in place of the nitrogen laser as the pump source for our LIF petroleum sensor. Roughly speaking, the energy needed for exciting the PAHs is inversely related to the number of rings so the shorter wavelength of the XeCl laser is able to more efficiently excite fluorescence in lighter fuels that contain only one and two ring PAHs, such as jet fuels, which have been difficult to detect using the nitrogen laser. The XeCl source also appears to improve the detection limit compared to the nitrogen laser system, perhaps due to stronger absorption at the shorter wavelengths. The effects of different excitation wavelengths on the measured spectral shapes for various fuel types is still under investigation. We will present the results of field investigations at various contaminated sites, as well as laboratory studies to compare the predicted performance of the XeCl and nitrogen laser based systems.

References

- [1]. General Accounting Office, "Hazardous Materials: Upgrading of underground storage tanks can be improved to avoid costly cleanups", GAO Report GAO/NSIAD-92-117.
- [2]. S.H.Lieberman, G. A. Theriault, S. S. Cooper, P. G. Malone, R.S. Olson, P.W. Lurk, "Rapid, subsurface, in situ field screening of petroleum hydrocarbon contamination using laser induced fluorescence over optical fibers", Proceedings of the Second International Symposium Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, NV, Feb 1991, pg 57-63.
- [3]. R. Neissner, A. Krupp, "Detection and chemical characterization of polycyclic aromatic hydrocarbon aerosols by means of laser induced fluorescence", Part. Part. Syst. Charact., 8, (1991), 23-28.

[Knowles, Lieberman, Davey, Wingfield, "Laser-Induced fluorescence spectroscopy..."]

- [4]. R.W.St. Germain, G. D. Gillispie, "Transportable tunable dye laser for field analysis of aromatic hydrocarbons in groundwater", Proceedings of the Second International Symposium Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, NV, Feb 1991, pg 789-792.
- [5]. J. W. Birks, **Photophysics of Aromatic Molecules**, Wiley Interscience, London, 1970.
- [6]. D.S.Knowles, S.H.Lieberman, "Field results from the SCAPS Laser-Induced Fluorescence (LIF) sensor for in-situ, subsurface detection of petroleum hydrocarbons", Proceedings of the European Symposium on Optics for environmental and Public Safety, Munich, Germany, June 1995.

^{*}presenter/corresponding author